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Seasonal variation of contaminant concentrations in wastewater treatment works effluents and river waters

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Abstract

Results are presented for 170 wastewater treatment works sites (20 per substance in influent, effluent and 36 per substance in river water upstream and downstream of the WwTW discharge) over a period of two years between 2015 and 2017; this comprises data for approximately 3,000 samples for effluent and 6,000 for river samples taken downstream of effluent discharges. Seasonal trends in contaminant concentrations for several substances are reported. Two clear patterns of seasonal variation are proposed over and above all of the variables associated with environmental data including process technology, dilution and geography. Firstly, variation of riverine concentrations caused by seasonal fluctuations in river flow (sewage flow being relatively consistent) resulting in summer maxima and winter minima. Alternatively, variation is observed that is attributable to the improved performance of wastewater treatment processes under warmer conditions. This leads to lowest concentrations in autumn when surface water/sewage treatment temperatures tend to peak. Seasonality for trace contaminants is more difficult to characterise than that of sanitary parameters owing to the higher variability in concentration of the substances of interest. The data also provide an insight into the amplitude of such variations. This makes it possible to assess the likely effects of seasonality and its impact on aquatic life. For example, the existence of seasonality (perhaps due only to dilution effects) might be demonstrated, but the amplitude might be too small in relation to the potential ecotoxicological effects to be of any consequence.

Key words: priority chemicals; effluents; seasonality; water quality; rivers

1. Introduction

In the UK on each day, approximately 347,000km of sewers collect 11 billion litres of wastewater; this is treated in approximately 9,000 wastewater treatment works (WwTW) that serve 96% of the UK population [1]. WwTW effluents thus constitute the main discharges to surface waters and, consequently, are the principal source of contaminant inputs to receiving river waters. Over the last 50 years, the water industry has made substantial investments in the improvement of wastewater treatment, principally in response to legislation including the Dangerous Substances Directive [2], Urban Wastewater Treatment Directive [3] and Water Framework Directive - WFD [4]. This has led to marked reductions in the discharge of the contaminants conventionally associated with sewage effluents, such as biochemical oxygen demand (BOD), suspended solids and ammonia. In more recent years, however, focus on pollution has widened to include a greater range of trace substance that did not feature in the original design criteria of treatment processes. Current concerns that are reflected in directives such as the WFD, now extend to over 50 substances, including metals, pesticides, industrial chemicals, solvents and other organic pollutants [5]. Reductions in concentrations of these substances in wastewater can be achieved by conventional treatment via biodegradation, volatilisation or adsorption to sludge solids. Indeed, for some contaminants removal mechanisms can be highly effective [6]; in other cases, further or enhanced treatment might be required.

Many exercises have been conducted to assess both seasonal and sustained longer term trends in environmental variables. This is particularly the case for nutrients such as phosphate and nitrate, BOD and ammonia, which are key determinands in assessing water quality status at specific sites and catchments owing to the availability of long term datasets for routinely determined parameters [7-9]. However, there is no overall analysis of seasonal trends taking account of aggregated data of a substantial number of WwTW in order to analyse the seasonality of treatment for emerging compounds such as pharmaceuticals or the generic influences of WwTW effluents on receiving waters for substances of high concern but for which routine data is rarely collected (i.e. for priority micropollutants chemicals known to be persistent, bioaccumulating and toxic).

Extensive monitoring over the past five years as part of the UK Water Industry Research (UKWIR) Chemical Investigation Programme (CIP) phase 2 (described as CIP2 from here onwards) has played a key role in the selection of substances and sites for future controls and remedial measures [10,11]. The most recent elements of the CIP2 are scheduled to report on effluent and river quality at over 600 sewage works in the period 2015-2020. Seasonal variation in contaminant concentrations in sewage effluents and river waters impacted by effluents can be an important

feature of interest in this context. An understanding of seasonality is important if monitoring is to provide accurate information on which to base water quality management decisions. Otherwise, there is the potential for programme outputs (for example annual average concentrations) to be biased, thereby calling into question the validity of the assessment of environmental quality and compliance with standards.

Seasonality can also be of interest for several other reasons. Environmental impacts of contaminants might only be of concern if the highest concentrations of contaminants coincide with the seasonal presence of sensitive species or aquatic life stages in the surface water of interest. Furthermore, various unsupported assumptions are often made regarding the nature of seasonal trends (for example, that antibiotics or analgesics might be present at higher concentration in winter or, conversely, that higher river flows in winter will reduce concentrations below those that prevail in summer); such assumptions are rarely quantified or fully supported by reliable evidence. The 2015-2017 output of CIP2 data provides a source of high quality analytical data over two years of sampling for 170 WwTW and associated downstream sites across the whole geographic area of England. This paper summarises findings on the basis of seasonality, through an analysis of results for up to 6000 samples, collected across of England and Wales. Determinands include nutrients, sanitary parameters (BOD, ammonia) as well as a range of priority substances regulated under the Water Framework Directive for which no previous seasonal patterns of environmental distribution has been analysed. Furthermore, the density of the dataset has allowed conclusions to be drawn regarding seasonal trends without the need to access data on flows, temperature and catchment characteristics. Access to such a substantial dataset facilitates the illustration of trends and allows conclusions to be drawn regarding the occurrence and magnitude of seasonal variation at an overall national scale. It should be noted that whilst compliance levels with water quality standards are important and are discussed elsewhere [12], this is not the focus of this paper and is therefore not a major feature of the discussion below.

2. Methodology

2.1 Substance selection

The complete CIP2 programme included up to 73 individual determinands including dissolved and total metals (not considered here), priority hazardous substances, priority substances and specific pollutants identified under the Water Framework Directive, nutrients such as nitrate, phosphate (soluble and total), ammonia, biochemical oxygen demand, chemical oxygen demand, total suspended solids, pH, dissolved organic carbon and major ions. Not all determinands were analysed in all samples, pharmaceuticals were only determined in influent and effluent from WwTW. A full list

of determinands included within CIP2 are provided in Table S1. The data reported here are for a subset of substances covering sanitary determinands (BOD, ammonium ion), nutrients (soluble reactive phosphate), priority hazardous substances under the WFD (perfluorooctane sulphonic and octanoic acids: PFOS, PFOA respectively; hexabromocyclododecane: HBCDD; cypermethrin and benzo-a-pyrene in effluent and receiving waters. Furthermore, the seasonal trends of the pharmaceuticals ethinyloestradiol, a hormonal steroid, the antibiotic, erythromycin, and the non-steroidal anti-inflammatory drugs ibuprofen and diclofenac (the former available over the counter and by prescription, the latter prescription only) in WwTW influent and effluent were assessed. These 12 chemicals were selected to be illustrative of certain types of substance characteristics as well as seasonal trends associated with either WwTW efficiency or river dilution patterns. A full analysis of all 73 CIP2 determinands was beyond the scope of this assessment.

2.2 Sampling

Results to date have been processed for 170 WwTW sites (20 occasions per substance in effluent and 36 per substance in river water upstream and downstream of the effluent discharge – Table 1) over a period of two years between June 2015 and June 2017 across the whole of England (Figure 1). Numbers of results per substance therefore corresponded to over 3000 for effluent and over 6,000 for river samples taken downstream of effluent discharges, outside of the mixing zone [13] at the nearest practical bridge access point.

Samples were collected as random, single grab samples using clean telescopic dipper systems off bridges in the middle of the flow from below the surface of the water. Sampling equipment was acid and/or decon cleaned prior to use and rinsed thoroughly with sample (at least 3 times) prior to collecting the sample for processing. Samples were taken at approximately evenly spaced time intervals over the two-year sampling period, rather than as composite sampling. This latter approach was precluded by concerns about sample stability raised in tests prior to the commencement of the programme [14]. There are no internationally agreed specifications for determining when to take samples during the course of a working day or week. However, it is widely accepted that taking samples between working hours from Monday to Friday may not lead to a truly representative estimate of the effluent or water at that site [15]. Therefore as a pragmatic and practical target, a minimum of 15% of sampling was undertaken in non-working hours (evenings and weekends) which was a sufficiently high frequency to account for any possible bias in the sample collection process; whilst being practical in terms of staff availability and gaining access to sites (for WwTW sample collection).

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Table 1 Summary of data used for this analysis

CIP2 Driver Code	Name	Sample type	Total samples per site	Samples per sampling occasion	Substances*	Comments
C1a	Further effluent characterisation	Effluent from the works	20	1 sample at each of 20 events	Metals, P(H)Ss, sanitaries	Sampled at same time as C1e
C1b	Emerging substances	Influent and effluent to the works	20	1 sample at each of 20 events	Pharmaceuticals and sanitaries	Sampled at same time as C1a
C1e	River sampling	Upstream and downstream of effluent discharge	36	1 sample at each of 36 events	Metals, P(H)Ss, sanitaries	Sampled at same time as C1a

* P(H)S = Priority and Priority Hazardous Substances under the Water Framework Directive

Sanitaries = BOD, ammonium ion, Chemical Oxygen Demand, suspended solids

149

150

151 **Figure 1 Location of sampling sites for CIP2**

152

2.3 Sample treatment and analysis

The samples were collected in stainless steel samplers, stored in glass containers and transported at 4° C to the analytical laboratories. The maximum sample storage period was determined for key determinands prior to the beginning of the programme by undertaking tests of sample stability. A period of 3 to 5 days storage for trace determinands (depending on substance) was shown not to lead to more than a 20% change in concentration. Detailed sampling, filtration and preservation requirements are provided in S2. Analytical work was commissioned from contracted laboratories, who used their own in-house analytical methodologies, which were not standardised but had to meet a minimum and exacting performance criteria. Given the variety of potential methods used and allowing for commercial sensitivities it is not possible to detail specific Gas and/or Liquid Chromatographic-Mass Spectrometry techniques employed by the laboratories. However, to ensure analytical quality was paramount the programme management team demanded a number of criteria for laboratories to meet before participating. This included ISO17025 accreditation, the requirement to undertake tests of analytical performance to demonstrate that they met the stated programme requirements for limit of detection (LOD), precision and recovery in relevant sample matrices at relevant concentrations (Table 2, S1) that is, proof of performance was required, rather that methods being stipulated. See section S1 and Table S1 of the electronic supporting information for more detail.

Table 2 Determinand abbreviations, required limits of detection and total error for WFD priority chemicals assessed

Code	Determinand	Required LOD effluent	Required LOD river	P % (i)
PFOS	Perfluorooctane sulfonic acid (µg/l)	0.00065	0.00009	50
PFOA	Perfluorooctanoic acid (µg/l)	0.00065	0.00009	50
HBCDD	Hexabromocyclododecane (µg/l)	0.0016	0.00023	50
BAP	Benzo(a)pyrene (µg/l)	0.00017	0.00002	50
CYP	Cypermethrin (µg/l)	0.00008	0.00001	50
DCF	Diclofenac (µg/l)	0.01	0.01	50
IBPF	Ibuprofen (µg/l)	0.01	0.01	50
EE2	17α ethinyloestradiol (µg/l)	0.00003	0.00003	50
ERMY	Erythromycin (µg/l)	0.1	0.1	50
AMON	Ammoniacal nitrogen (as N) (mg/l)	0.1	0.1	50
BOD	Biochemical Oxygen Demand (mg/l)	2	2	50
TP	Total phosphorus (as P) (mg P/l)	0.01	0.01	50
SRP	Soluble reactive phosphate (as P) (mg P/l) (filtrable (0.45 µm pore size) and molybdate reactive phosphate	0.01	0.01	50

[1] P% is the target maximum tolerable error and is equal to:

$$\left[(targetLOD)^2 + \left(\frac{A \times P\%}{100}\right)^2\right]^{\frac{1}{2}}$$

177 Where the target maximum LOD and P% are given in the Table 1 and A is the determinand concentration in the sample.
178
179 Performance testing was designed to demonstrate that the tolerable total error limit is achieved by
180 showing that precision (2 x standard deviation) and bias was respectively no larger than half the
181 target maximum total error. Thus, for example, for a total tolerable error limit of 100 units, standard
182 deviation should be shown not to be larger than 25 and bias should not exceed 50. The LOD was
183 defined as 3.3x the standard deviation of blank-corrected results of determinations made on a
184 sample containing essentially no determinand (where possible in a relevant sample matrix) [16]. In
185 some cases, it was not possible to find effluent samples free from determinands in which case a
186 synthetic sample was used.
187
188 Within laboratory QC analyses were undertaken for both laboratory tests and field sampling.
189 Laboratories also took part in a bespoke proficiency testing scheme. Details of the proficiency testing
190 scheme used to confirm data quality is provided in S1 of the Electronic Supplementary Information
191 (ESI). Where reported concentrations were below the required LOD, the result was substituted at
192 half face value - as stipulated in the relevant Directive [17]. As part of the proficiency testing scheme
193 Z scores were calculated. A Z-score is a numerical measurement of a value's relationship to the
194 mean in a group of values. If a Z-score is 0, it represents the score as identical to the mean score.
195 Z-scores may also be positive or negative, with a positive value indicating the score is above the
196 mean and a negative score indicating it is below the mean. Positive and negative scores also reveal
197 the number of standard deviations that the score is either above or below the mean [18]. Of the
198 approximately 250 z-scores calculated for the above pharmaceuticals tested there were only eleven
199 instances of z-scores greater than 2. Of these only three were larger than 3 (rated as
200 “unsatisfactory”). There were no instances of continued or consistent patterns of error. Hence
201 proficiency test results indicate a very positive picture, with CIP laboratories performing to a high
202 standard with respect to CIP requirements. Consequently, it was concluded that for the substances
203 considered here, there were no important instances of inter-laboratory bias or inter-regional variation
204 (data not shown), which would indicate important bias in the methodology of sample handling and
205 analysis.

206
207 The approach to the assessment of seasonality was to list all reported results for a given determinand
208 in order of sampling date, to group the resulting string of data into monthly sets and to calculate the
209 mean and 90% confidence interval for each month (combining information of a given calendar month
210 in each of the two years of sampling). Results were also in some cases assessed as single series
211 over the sampling period to examine whether or not an annual variation was repeated over the two
212 years of sampling.

2.4 Data analysis principle and methodology

The purpose of the analysis carried out on this dataset was to determine whether or not seasonal trends could be observed using measured concentrations alone, independent of environmental variables such as dilution in the river, temperature affecting WwTW performance, time of sampling, type of WwTW etc. In order to undertake this analysis it was necessary to condense the large dataset into monthly averages to achieve this a Locally weighted scatter-plot smoother (LOESS) smoothing curve [19] was plotted where appropriate. The results of this analysis are shown below. Values plotted are monthly averages (of approximately 300 results for effluents and 500-600 results for river waters) with an associated 90% confidence interval.

3. Results and discussion

Samples were collected from 170 sites across the whole of England from Pegswood in Northumberland to Fraddon in Cornwall, a distance of approximately 750 km, encompassing large (e.g. Thames, Severn and Humber) catchments as well as much smaller rivers where previous assessments have considered WwTW to have a potential impact on downstream contaminant concentrations. Sampling not only covered geographic extent and catchment size, but also widely varying geology (chalk through to granite), demographics (urban to rural) and climatic conditions (Figure S1). WwTW size sampled varied from serving a population of less than 1,000 to almost 1.5m. Average dilution of the CIP2 WwTW varies but sites were selected on the basis of likely to have lower dilution and hence a higher priority for monitoring the impacts of effluents on receiving waters. A mean estimated dilution from previous work was approximately 150 times but the median much lower at around 8 times dilution [20]. Met Office data [21] for the whole of England suggests that 2016 was a slightly warmer (mean of 10.2 vs degrees Celsius) than the long term trend but typical for overall average rainfall (821mm).

By aggregating and analysing the full data it was possible to examine concentrations across the sampling period to determine trends in concentrations which might therefore have an impact on reported annual averages against environmental quality standards as well as assessing the magnitude of impact that WwTW may have on downstream observed concentrations. This approach of plotting monthly data provides three clear types of annual profiles associated with seasonal trends in observed concentrations within river water receiving WwTW effluent. These trends may be explained in the following way:

Type A: concentrations influenced primarily by in-river dilution rather than WwTW treatment efficiency;

Type B: concentrations that follow seasonal (largely temperature-based) WwTW efficiency patterns;

Type C: concentrations with relatively seasonally invariant patterns

Although quite simplistic in concept, dividing the observed trends up into these three types is designed to illustrate the potential significance of impact a WwTW effluent might have on observed downstream concentrations. The data analysis shows that in fact for some substances discussed below, it is the performance of the WwTW (largely related to temperature changes and hence microbiological activity and/or efficiency) which determines the observed seasonal profiles, not environmental factors such as in-river dilution.

Although a full analysis of river flows associated with each individual WwTW would be helpful in determining dilution factors available, obtaining such data for 170 WwTW locations across catchments extending across the whole of England was far beyond the scope of this project. Such data have formed part of the source apportionment analysis detailed elsewhere [20]. Suffice to say, the general pattern of seasonality in river flow in the UK is well established and reported [22] with higher flows during winter months (December to February) compared with summer (June to August) although regional variations occur. A degree of dilution of wastewater may occur within the sewer system after periods of rain owing to some sewer catchments collecting both domestic and industrial wastewater as well as runoff from rooves and roads (termed combined sewers). In fact, within some catchments there is a mix of both combined and separated sewerage within the same urban catchment, with combined sewers within the older urban centres and separated systems in newer satellite housing estates [20]. Furthermore, some temperature trends across the UK could have also impacted on works efficiency but have not been allowed for because the point of this data analysis exercise has been to use a sufficiently large chemical analysis dataset to absorb these influences and therefore to determine seasonal trends which are over and above such variables.

3.1 Type A: Seasonal trends determined by dilution

This is illustrated with reference to phosphorus concentrations. WwTW sources, along with diffuse agricultural runoff, are the principal phosphorus inputs to surface waters [20]. Elevated concentrations are a major cause of Environmental Quality Standard (EQS) exceedances under the

WFD [23]. Understanding relative contributions and seasonality is vital as phosphorus concentrations and standards are linked to biological activity which is itself seasonally mediated. Figure 2 provides a LOESS fit for SRP in river samples downstream of effluent discharge over two years.

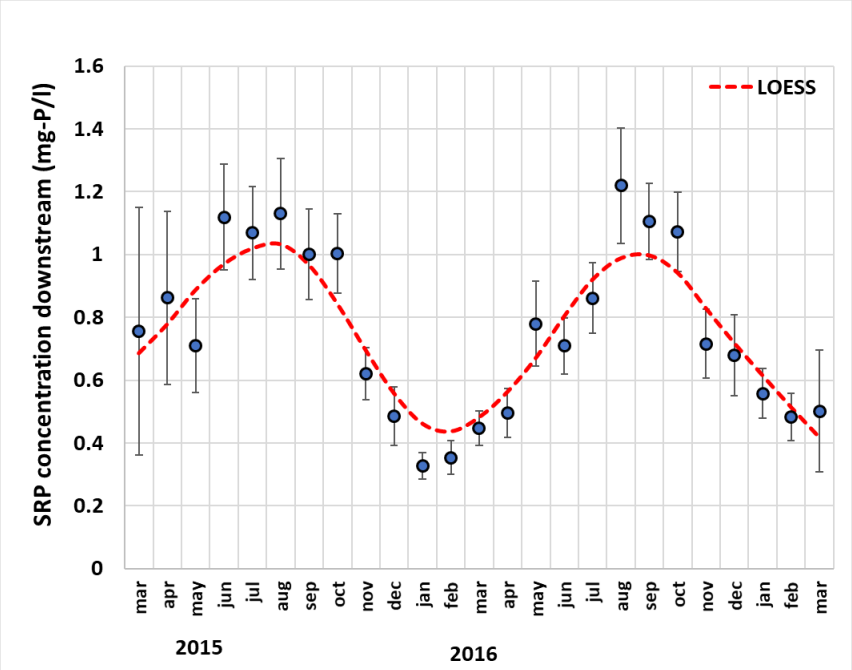


Figure 2 Soluble reactive phosphorus in river samples downstream of effluent discharge over two years (averages with a 90% confidence interval)

Soluble reactive phosphorus concentrations show marked seasonality within downstream receiving waters. Highest concentrations were observed in later summer and lowest in later winter. This picture is consistent with relatively constant emission of phosphorus from WwTW over an annual period, with mean monthly concentrations for all 170 WwTW effluents only varying between 1.7 and 2.5 mg-P/l over the sampling period, compared with a variation of a factor of 3 (ca. 0.4 to 1.2 mg-P/l) for observed downstream river concentrations (Figure S2).

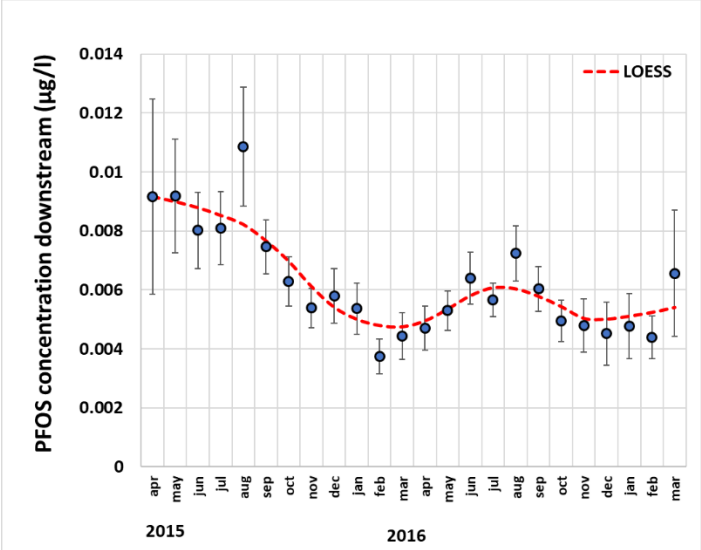
Some of the observed limited variability of WwTW SRP concentrations reflects that a large proportion of the WwTW (in this case approximately two thirds of the 170 sampled) have discharge permits applied to their effluents; restricting concentrations to an annual average of typically 1 or 2 mg-P/l. Works without explicit measures for phosphorus removal, have effluents of concentration of around 5 mg-P/l [24]. The lower concentration of P present in the WwTW effluent during winter months is most likely to reflect the increased proportion of surface water runoff low in P from combined sewers entering the WwTW during wetter times of the year (e.g. Figure S3) rather than within WwTW

efficiency variation (see Type B below) because there is an excess of P entering WwTW over and above that required to maintain works performance [25,26].

Recent trend analyses have been carried out for P in the UK [7-9] using long term datasets. They have assessed the wider catchment influences including WwTW, which also recognise the asynchronous relationship between river flow and observed concentrations associated with predominantly low flows in summer and higher flows in winter (for example see Thames river flows in Figure S3). Changes in amplitude of the seasonality and slight shifts in synchronisation were attributed to changes in WwTW effluent quality and long term decline in fertiliser use on agricultural land. It may be concluded therefore that variation in available dilution of effluent derived P in receiving waters significantly exceeds variation in seasonal effluent concentrations.

Analysis in-river data downstream of WwTW effluent discharges for priority chemicals regulated under the WFD there is evidence that perfluorinated octane sulphonic acid (PFOS), perfluorinated octanoic acid (PFOA) and hexabromocyclododecane (HBCDD) fall into Type A patterns. Figure 3 shows PFOS, PFOA and HBCDD averages by calendar month respectively. Prior to extensive source control, all three compounds were used extensively in products and as flame retardants owing to their thermal stability, which is an important factor in their persistence in the environment, leading to bioaccumulation and concerns regarding toxicity and food chain transfer.

PFOS was originally included in REACH annex xvii restricted substances list. After PFOS was added to the Annex B of the Stockholm Convention in 2009, the European Commission removed PFOS from REACH annex xvii and added it to the annex I of the Regulation (EC) No 850/2004 of the European Parliament and of the Council on persistent organic pollutants. PFOS is now regulated as a persistent organic pollutant (POP) in EU [27]. Consequently, it is limited to less than <10 mg/kg in products and preparations, <0.1 % by weight calculated with reference to the mass of structurally or micro-structurally distinct parts that contain PFOS, <1 µg/m^2 of the coated material in textiles or other coated materials. Exemptions occur for photoresists or anti reflective coatings for photolithography processes, photographic coatings, provided certain conditions are met.



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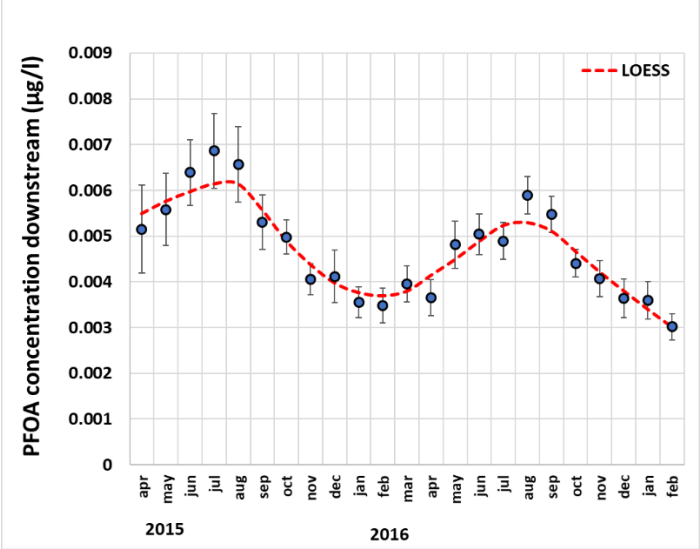

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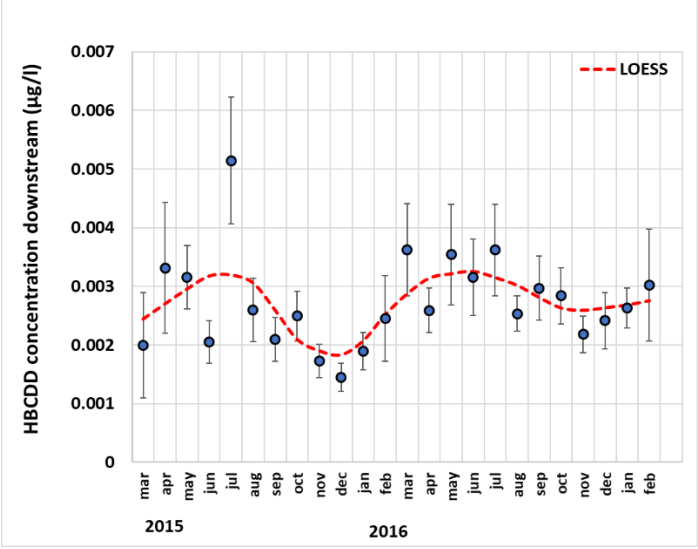

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338 **Figure 3** **PFOS (top graph), PFOA (middle graph) and HBCDD (bottom graph) in river**
339 **samples downstream of effluent discharge over two years with LOESS plot**
340 **(averages with a 90% confidence interval)**

Perfluorooctanoic acid (PFOA) and its salts are suspected to have a similar hazard profile to PFOS, estimates of 100's to low 1,000's of tonnes per year use in the EU have been calculated with a high degree of uncertainty [28,29], which appear to be less than that for PFOS. PFOA was added to REACH annex XVII restricted substances (entry 68) by Commission Regulation (EU) 2017/1000 on 14 June 2017. Requirements include that it shall not be manufactured, or placed on the market as substances on their own from 4 July 2020; shall not, from 4 July 2020, be used in the production of, or placed on the market in (a) another substance, as a constituent; (b) a mixture; (c) an article, in a concentration equal to or above 25 µg/kg of PFOA including its salts or 1000 µg/kg of one or a combination of PFOA-related substances. A number of exemptions apply through to 2032 [30]. Control over the production and use of these substances means that concentrations should be decreasing in the environment, although sources are most likely to be associated with WwTW with the exception of inputs from release of firefighting foams directly into the environment, as was the case with the Buncefield fire in the UK in 2005 [31].

The prevalence of these compounds in the products and their persistence means that they are still detectable, and the fact that they are resistant to degradation means they will be less impacted by seasonal changes in WwTW efficiency and observed river concentrations will be controlled by river dilution. Two-year trends for samples collected downstream of WwTW for PFOS (Figure 3) show minima during December and January for the two years. The EQS for PFOS is 6.5×10^{-4} µg/l as an annual average [32] and so concentrations in the river downstream of the WwTW are still of the order of 10 times the compliance target, at any given time of the year (across all sites in England and Wales downstream of WwTW). Consequently, any observed seasonality combined with frequency of compliance monitoring schemes, will not impact on the observed compliance for this substance.

PFOS has been reported in river samples downstream of WwTW in other countries such as Japan and USA where concentrations range from low ng/l as reported here up to 100's of ng/l, which is significantly higher [33-35]. The reported higher concentrations may be resulting from lower dilution, the fact that the data reported elsewhere is at least 10 years old (and so pre any possible restrictions) or potential contributions from surface runoff [35].

PFOA concentrations downstream of WwTW are of similar concentrations, but marginally lower, likely to reflect the lower volumes used within Europe. The PNEC assigned to PFOA is the same as the EQS value for PFOS (6.5E-04 µg/l) and so observed levels across England and Wales are just under 10 times the PNEC for any given waterbody at any time of the year. Seasonality shows the same trend (Figure 3) but with an amplitude that varies by about a factor of two, and is better defined than that for PFOS. For the same reasons of source and persistence, the observed concentrations

downstream are driven by dilution. As for PFOS, other reported concentrations in Japan and USA range from ng/l to 1000's of ng/l downstream of manufacturing facilities or sewage treatment works [33,34]. There was however, no assessment of seasonal patterns to compare with the UK data reported here.

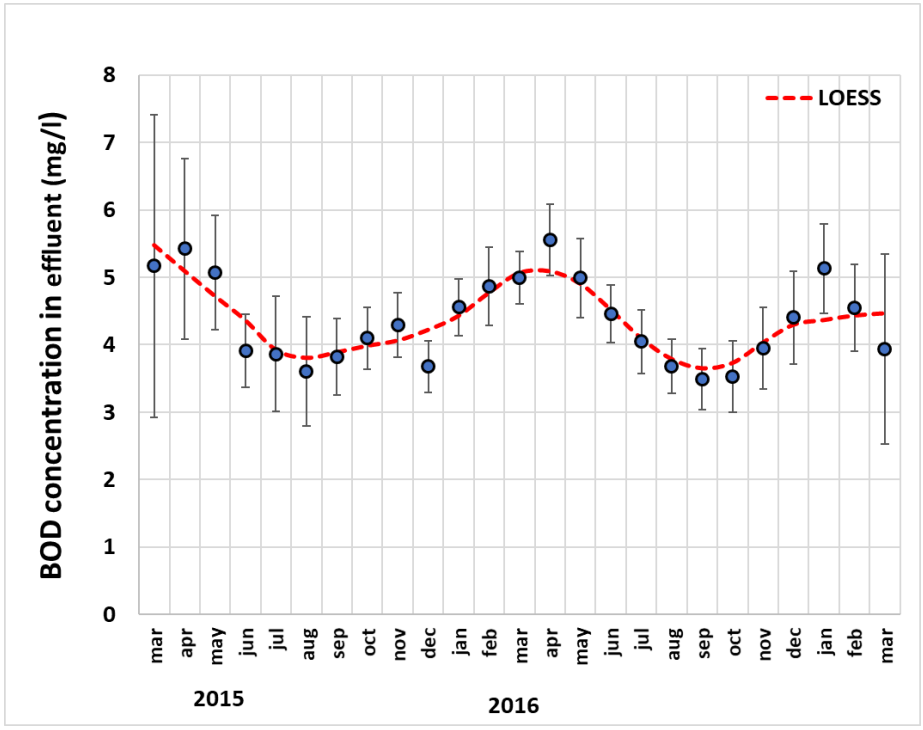
For HBCDD concentrations across all sites sampled throughout England and Wales are lower than PFOS or PFOA monthly concentrations, averaging around 0.0025 µg/l downstream of the 172 WwTW (Figure 3). The lower concentrations may reflect reduced production and use compared with PFOS/PFOA although a seasonal trend still is evident, the winter minimum in 2016 is less pronounced than that for 2015. The annual average EQS set for identified sites within waterbodies is 0.0016 µg/l and so again, seasonality and monitoring frequency/pattern will not impact on compliance assessments for these sites as observed concentrations are almost exclusively greater than the EQS. The limited data reported from other sources shows HBCDD levels are similar, for example, effluent concentrations ranged from 0.4 to 12 ng/l in WwTW effluents and 0.19 to 14 ng/l in river samples, therefore of the same order as reported here for the UK [36].

3.2 Type B: Seasonal trends determined by treatment efficiency

Before discussing trends in treatment efficiency, it is important to note that the statistical analysis has been undertaken using all CIP WwTW for which data are available. There has been no attempt to split WwTW into different treatment types for a number of reasons. Firstly, sub dividing the dataset weakens the power of the statistical analysis and so detracts from the objective of determining statistically seasonal trends based on big datasets and secondly previous data has shown that any variation between works was not shown to be statistically significant [6].

Biochemical Oxygen Demand (BOD) is a key metric for water quality (Figure 4). The seasonal profiles for BOD are almost in complete opposition to those seen for SRP. Although clear seasonality is observed, its phase, with minima in early autumn and maxima in late winter, is the reverse of that for SRP. Furthermore, the amplitude of the variability is considerably greater in effluent than in river samples (again opposite to the behaviour observed for SRP), indicating a source of variation in the wastewater treatment process, and one that is powerful enough to reverse the effect of in-river dilution. This source of variation is proposed as the temperature dependence of the biological treatment process. During the warmer late summer/early autumn period the temperature and hence efficiency of BOD removal is at its highest, compared with winter where the opposite is the case [37]. This assumption is supported by data from further north, where under more Arctic conditions winter temperatures drop significantly below zero Celsius and impacts on WwTW efficiency has also been

413 reported [38]. There are unlikely to be significant variation across the English geographic regions,
414 because winter temperatures between the extreme north and south of the UK only vary by 2 degrees
415 Celsius (Met Office data).
416



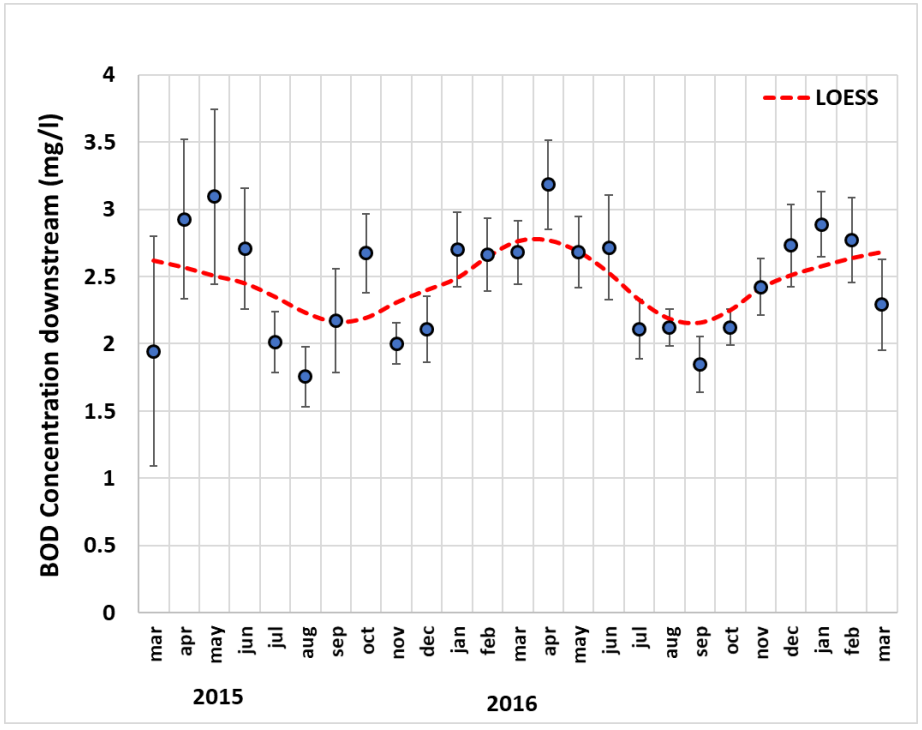


Figure 4 **BOD in WwTW effluent (top graph) and downstream (bottom graph) over two years (averages with a 90% confidence interval)**

Ammonia also exhibits a Type B behaviour similar to that for BOD, where reduced treatment efficiency in winter leads to higher concentrations observed downstream even when greater dilution occurs through the winter months (Figure 5). For good status under the WFD depending on typology (upland, lowland, high and low alkalinity) 90^{th} percentile concentrations range from 0.3 to 0.6 mg/l total ammonia (0.25 mg-N/l and 0.49 mg-N/l respectively). It is not possible to compare these values directly with an EQS because of the aforementioned aggregation of England and Wales data and the fact that compliance is based on a river typology and reported 90^{th} percentile concentrations. The influence of WwTW effluents on downstream concentrations is obvious for the UK, however, in rural environments where effluents are not a significant source of river flow, then observed concentrations tend to reflect a flow-based pattern, such is the case for the North Saskatchewan River, Canada [39].

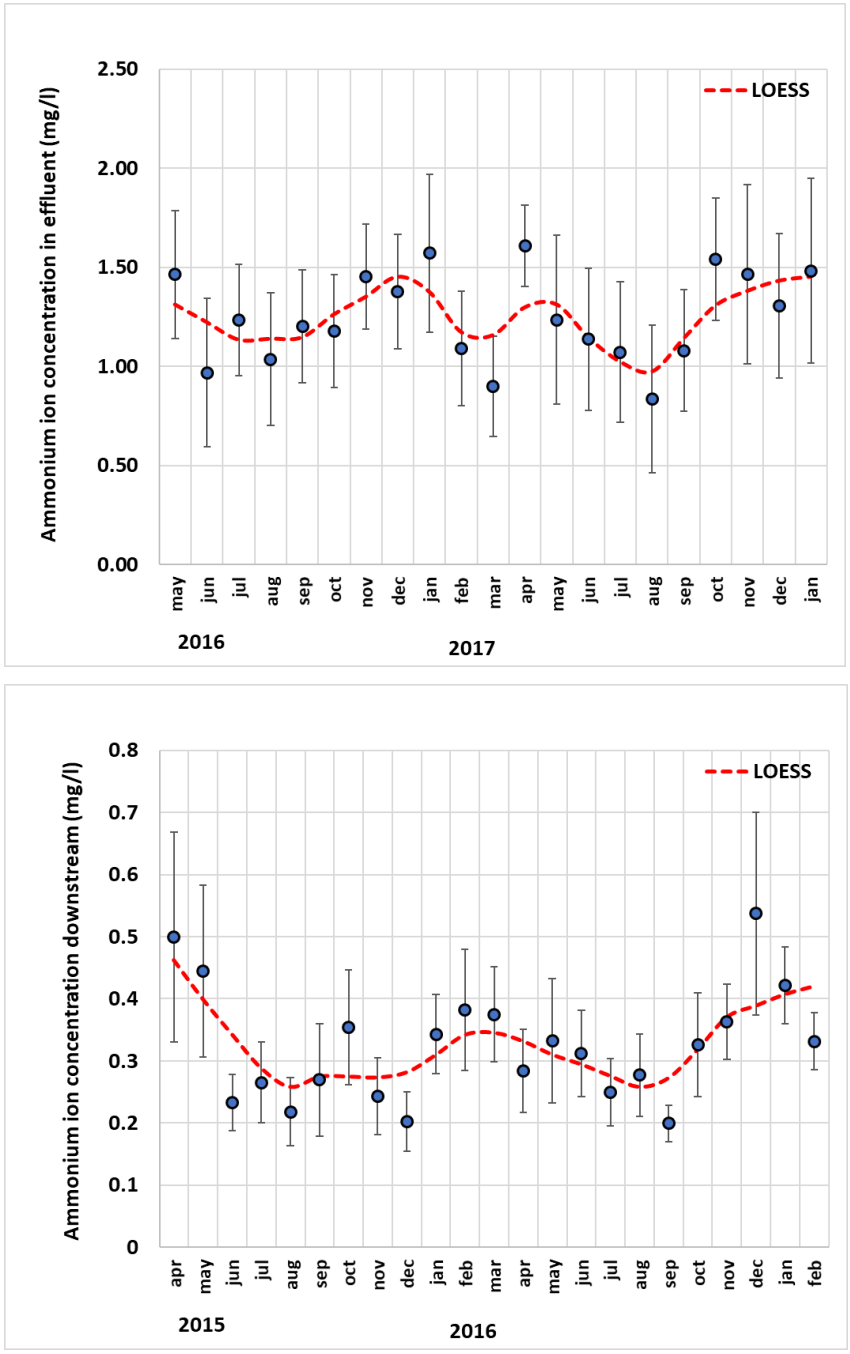


Figure 5 **Ammonium ion concentrations in effluent (top graph) and in downstream river samples (bottom graph) over two years with LOESS plot (averages with a 90% confidence interval)**

3.3 Type C: Little seasonal variation

Other priority substances exhibited limited seasonal variation (Type C) in terms of obvious and statistically robust conclusions. Cypermethrin for example (Figure 6) showed no statistically relevant trends at 90% confidence level.

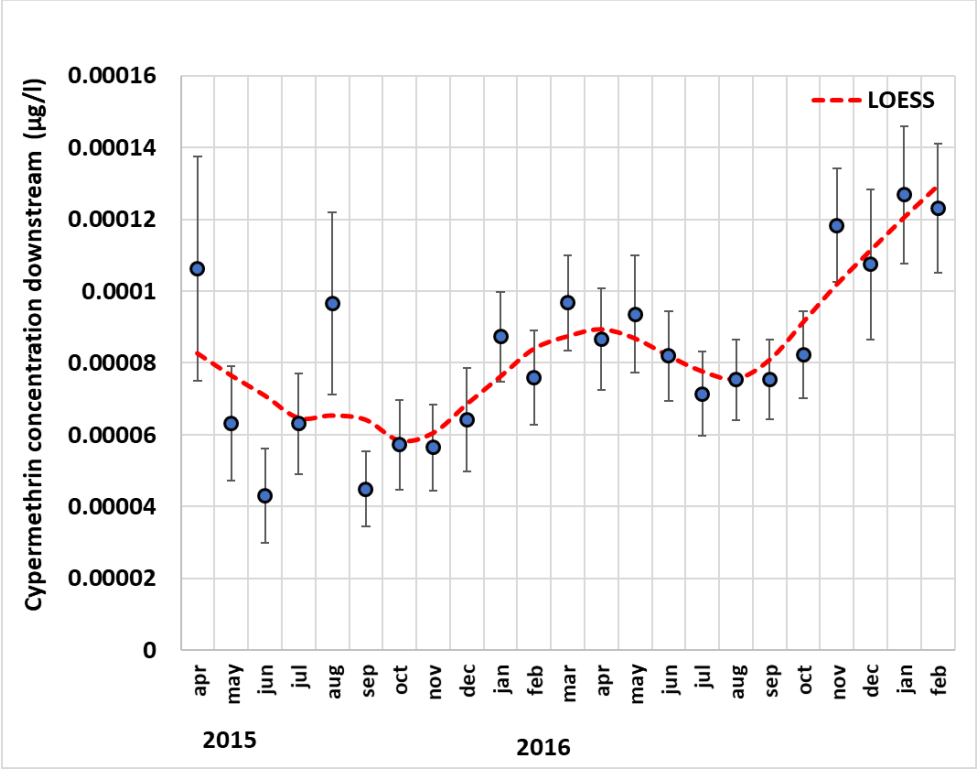


Figure 6 Cypermethrin in river samples downstream of effluent discharge over two years with LOESS plot (averages with a 90% confidence interval)

A further potential driver of seasonality, illustrated below by benzo(a)pyrene (Figure 7), should not be neglected. This is the case of substances for which the inputs to surface waters might vary, but for which WwTW effluent is not the primary source. Low concentration in the summer months are not related to sewage inputs and could probably be ascribed to seasonally reduced rainfall and consequent more limited influence of run-off as an input to rivers [40]. The EQS is 1.7×10^{-4} µg/l and so observed concentrations exceed the EQS by over 50 times largely as a result of diffuse runoff sources [41].

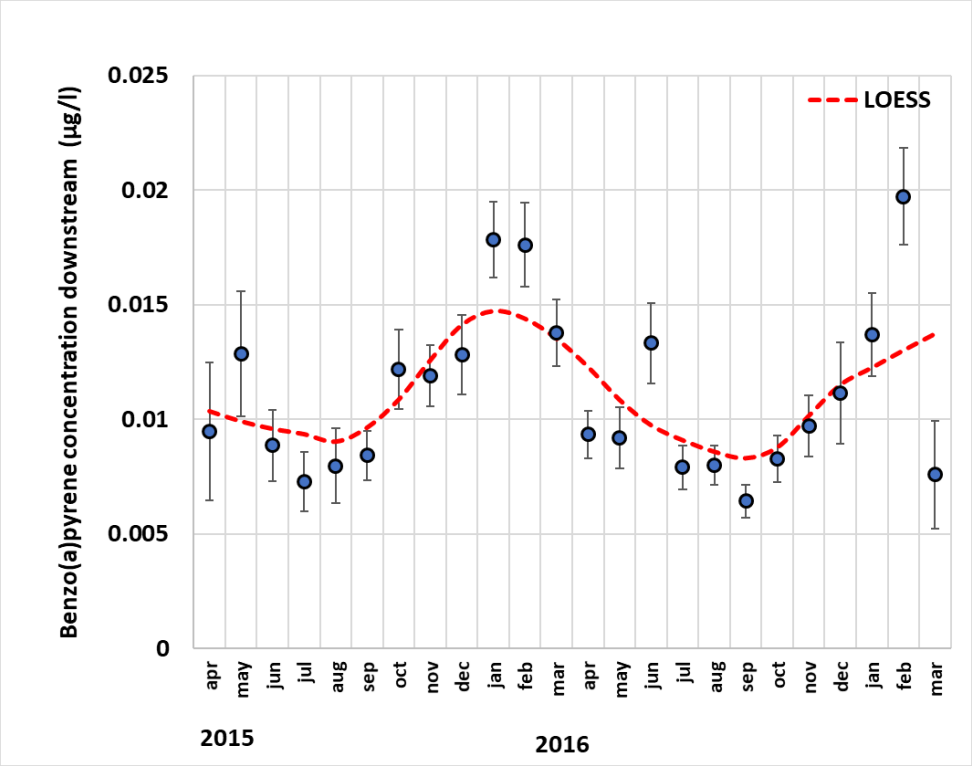


Figure 7 Benzo(a) pyrene in river samples downstream of effluent discharge over two years with LOESS plot (averages with a 90% confidence interval)

The CIP monitoring has shown that sewage effluents are not the principal sources of PAHs. Current opinion is that the main source in the UK is related to soils and surface waters contaminated by combustion products [42]. Given this, it might be proposed that run-off from soils and urban surfaces might be the main source and that lower volumes of run-off in the drier summer months could explain the seasonal effect illustrated above.

3.4 Seasonal trends in influent and effluent for pharmaceuticals

There is a dearth of data on seasonal trends for pharmaceutical concentrations within the environment. The ability to analyse the CIP2 data provides vital information for wastewater undertakers and regulators in terms of being able to plan future management strategies. Figure 8 below shows seasonal assessments for four pharmaceuticals representative of three large classes of popular medicines: a steroid oestrogen (ethinyloestradiol - EE2) where inputs to works may be expected to be constant year-round; two non-steroidal anti-inflammatory drugs (NSAIDs - ibuprofen and diclofenac) where again seasonality would not be expected in use [38] and an antibiotic (erythromycin) which could be expected to be more prescribed during winter months [43]. These substances were determined in both wastewater influent and effluent (but not in receiving river water). The volume of data for pharmaceuticals was not as substantial as for the determinands discussed above; results were obtained for 45 sites instead of 170. Figure 8 illustrates, by the differences in concentration in influent and effluent, the overall extent by which wastewater treatment reduces concentrations of each determinand and provide an indication that seasonality is not a particularly important factor in determining the concentrations of these substances either in influent or effluent. This suggests the assumption that NSAIDs and steroid hormones are consumed at a fairly constant rate throughout the year with few peaks or troughs in influent concentrations appears to hold true. There was, however, no significant pattern in the influent concentrations observed for erythromycin, which as an antibiotic, may lead to the assumption that there would be more prescription in winter than summer and hence increased influent concentrations during the winter months. Prescription data for macrolides such as erythromycin in America have shown seasonal trends in prescriptions of macrolide drugs [44]. In the UK, erythromycin is not used as a flu vaccine that is widely administered and is predominantly used for bacterial infections and is not effective against colds, flu or other viral infections and so may not necessarily be expected to follow a seasonal trend. Examination of effluent concentrations of the pharmaceuticals also fail to show a seasonal trend. This may be owing to the fact that many pharmaceuticals are either readily biodegradable such as EE2 and ibuprofen or poorly degradable such as diclofenac and erythromycin and so temperature has only a limited impact on removal. In colder climates such as Finland, a distinct reduction in removal has been reported for pharmaceuticals such as ibuprofen, diclofenac and naproxen in the winter months [38]. However average winter temperature in Finland are sub-zero Celsius compared with 6.8 Celsius for the UK (Met Office data).

The notable feature of data for all four substances is that there is little seasonal variation; certainly, there is little that might be of practical importance. The real-time (sequential) results for ibuprofen in effluents appear to be influenced by some high measured values early in the monitoring programme.

There is no indication of any seasonality for erythromycin either by calendar month or over the 2-year monitoring period. Finally, the time / concentration profile of the synthetic steroid EE2 is unusual in that the data for early 2015 appear to be higher than subsequent values, but there is a striking correspondence in the differences between the influent and effluent data; indicating a consistent reduction in concentration of two thirds during treatment.

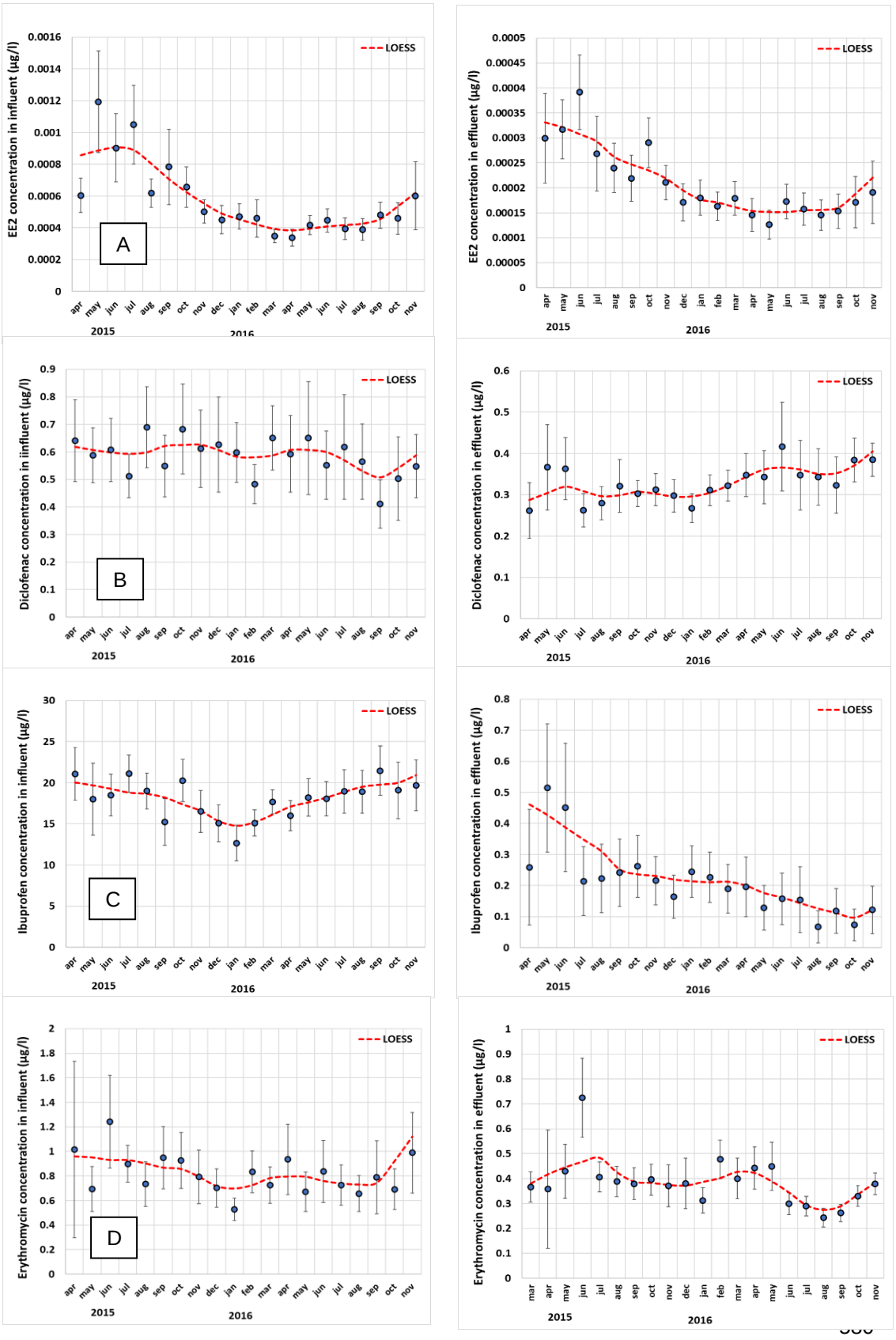


Figure 8 **Ethinylestradiol (A), diclofenac (B), ibuprofen (C) and erythromycin (D) in WwTW influent (left hand side) and effluent (right hand side) over two years with LOESS plot (averages with a 90% confidence interval)**

4. Conclusions

An analysis of over 6,000 samples has been completed to determine if it is possible to discern seasonal trends in observed receiving water concentrations and/or effluent and influent wastewater in the case of 4 pharmaceuticals. This has been the first time such a large dataset has been analysed for these substances, many of which are not routinely determined. Furthermore, it has been possible to show impacts that WwTW effluent has on downstream water quality irrespective of flow or climatic conditions. Seasonality has been observed in data for several determinands reported here. Two specific patterns driving seasonal variation within receiving waters are proposed:

a. Variation of riverine concentrations likely to be dominated by seasonal fluctuations in river flow (sewage concentration being relatively consistent). This appears to be responsible for a cyclic variation in riverine phosphate concentrations characterised by high concentrations in late summer and low concentrations in late winter;

b. Variation attributable to the performance of wastewater treatment rather than river flow and therefore subsequent dilution. Consequently higher concentrations are observed in colder months owing to less efficient wastewater treatment which is sufficiently to counteract any increase in dilution within the receiving water.

Seasonality for trace contaminants is more difficult to characterise than that of sanitary parameters owing to the higher variability in effluent concentrations and the significantly lower concentrations of the substances of interest leading to lower analytical precision. However, there is clear statistical evidence for in-river dilution on observed concentrations of PFOS and hexabromocyclododecane.

For pharmaceutical concentrations measured within WwTW (influent and effluent) no such seasonal cycling was observed, even for an antibiotic.

Overall, the data show not only the existence of seasonality (or lack of it), but also provide an insight into the amplitude of such variation. This makes it possible to use this type of mathematical modelling approach to assess the likely effects of seasonality in a wider context of regulation and potential impact on aquatic life. For example, the existence of seasonality (perhaps due only to dilution effects) might be demonstrated, but the amplitude might be too small to have any significant impact on either compliance monitoring bias or possible ecological effects.

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